Aging of Natural Resins in Presence of Pigments: Metal Soap and Oxalate Formation

Ageing of natural resins in presence of pigments: metal soaps and oxalates formation.

Tommaso Poli[1], **Anna Piccirillo**[2], **Marco Nervo**[2], **Oscar Chiantore**[1]

[1] Dipartimento di Chimica, Università degli Studi di Torino, Via Giuria 7, Torino, Italy, tommaso.poli@unito.it

[2] Centro Conservazione e Restauro "La Venaria Reale", Piazza Della Repubblica, Venaria Reale (TO), Italy

Abstract

The degradation process involving the formation of metal soaps in drying oils is a well-known problem due to the reaction of cations coming from pigments reacting with free fatty acids from the oil. A similar behaviour has been observed during an experiment concerning the aging of different natural resins (shellac, dammar and colophony) in the presence of common historic pigments (smalt, ochre, umber, azurite, lead white, zinc white and titanium white). In the case of natural resins, the terpenic acids react with the cations in the pigments. Each resin shows a different reactivity and affinity to different cations related to the complex mixture of terpenic structures and acids contained in natural resins. So far it has not been possible to identify one or more specific acids preferentially involved in this 'saponification' process. Colophony seems to be the most reactive resin while zinc white and smalt appear to be the most reactive pigments. The reason of a so different reactivity of the acid component of the three resin is unclear. Studies on acidity of different resins, free acid mobility and pigment reactivity are ongoing. Generally, the presence of a pigment has been proven to modify the stability of resins that have undergone accelerated ageing. Mixtures of resins and pigments have been exposed to natural and different artificial aging conditions (photo-oxidative, thermal, thermos-oxidative and wet).

Moreover, it has been observed that some pigments, particularly smalt and zinc white, favour the simultaneous formation of oxalates. The formation of oxalates and different degradation products from natural resins in the presence of pigments is particularly important, as it deeply affects the removability of varnishes and, more generally, the cleaning processes. Moreover, it permanently modifies the interface between painting and varnish layers as well as the aesthetic aspects of the paint surfaces.

Introduction

In the painting layers, the formation of carboxylic salts coming from fatty acids and the cations of pigments is a well-known issue (Meilunas et al. 1990; Boon et al. 1997; Lazzari and Chiantore 1999; Mallégol et al. 1999; Van Den Berg et al. 1999; Erhardt et al. 2000; Berg 2002; Colombini et al. 2002; Arbizzani et al. 2004; Dietemann et al. 2009; van den Brink et al. 2009). In particular, several studies have been published on the interaction between binding media, drying oils in particular, and metal salts (Boon et al. 2002; Noble et al. 2002; Higgitt et al. 2003; Plater et al. 2003; Keune and others 2005; Van der Weerd et al. 2005; Boon 2006; Cotte et al. 2006; Boon et al. 2007; Cotte et al. 2007; Mazzeo et al. 2008; Manzano et al. 2009). The effects of this transformation processes of the pictorial layer are different and not completely understood. Metal soaps may work as plasticizer of the film slowing the cross-linking (reticulation) processes and the embrittlement but also deeply affect the appearance and the state of conservation. Actually, free metal soaps molecules, in not well-clarified conditions, aggregate and migrate through surface creating protrusions or crusts. This new formations can determine the weakening and sometimes failures on the pictorial film (Boon et al. 2002; Boon 2006). The causes of the metal soaps formation reported in literature are many but humidity seems to play a key role.

In this study metal soaps formation has been verified in reproduced painting film of natural resin (shellac, dammar and colophony) mixed with some common pigments (smalt, ochre, umber, azurite, lead white, zinc white and titanium white) and compared with the results obtained using stand oil as binder. Natural resins are historically and widely, employed as finishing layers or varnishes, for their appreciated optical and preservative properties. In many cases, they have been used mixed with drying oils in order to obtain oleo-resinous binders with particular aesthetical properties, or else pure as binders in retouching paintings (Gunn et al. 2002). In all these conditions the resins, and in particular the terpenic acid fraction, come in contact with pigments by direct mixing or by interaction with the underneath painting layer often impoverished by natural binder migration and oxidation. Moreover, the usual conservation treatments require varnish substitution and fresh natural resin application in contact with a binder depleted painting layer as consequence of previous solvent-based cleanings. Nevertheless, very few studies (Carlyle 2001; Arbizzani et al. 2004; Doménech-Carbó et al. 2006) are present on the reactivity of natural resins with pigment and mostly related to the verdigris (copper acetate) and copper resinate recipes. This paper report and summarize the results of a systematic study on the formation of metal soaps in presence of natural resins (Poli et al. 2017). Shellac, even if lesser used in easel paintings, has been chosen in order to evaluate the influence of the mobility of terpenic acids in the soaps formation. Shellac contains a large reticulate fraction due to the presence of aleuritic acid that it supposed to reduce the terpenic acids mobility. The mock-ups were then artificial aged (thermal and photo oxidative ageing) and analysed by mean of FTIR technique in transmission and imaging mode. This experimentation started from some consideration on three case studies (here presented) where metal soaps and oxalates have been found

in presence of natural resins. The formation of oxalates and different degradation products from natural resins in the presence of pigments is particularly important, as it deeply affects the removability of varnishes and, more generally, the cleaning processes. Moreover, it permanently modifies the interface between painting and varnish layers as well as the aesthetic aspects of the paint surfaces.

Materials and methods

A mixture of pigment and binder (2:1 w/w) has been applied on glass microscope slides and on silicon wafers for the imaging measurements.
Azurite, lead white, titanium white, zinc white, red ochre and raw umber pigments were purchased by Kremer Pigmente, Germany. Smalt has been purchased by Zecchi, Italy. Stand-oil (linseed oil heated in absence of oxygen), colophony, dammar and shellac were purchased by Kremer Pigmente, Germany.
Five sets of samples have been prepared and differently aged in five different ways:

- 3 years at room condition with no direct sunlight exposition (22° and 55%RH)
- a total of 1000 hours (with an intermediate step of 600 hours) in oven at 50 C° (20% RH)
- 1000 hours of simulated solar irradiation in an UV solar box Hereus Suntest CPS equipped with a filtered (coated quartz glass simulating a 3 mm window glass, cutting $\lambda<300$ nm) Xenon lamp and with an average irradiation of 750 W/m^2 and an internal temperature of about 50 C°.
- wet (3 days) and dry (7 days) alternated cycles up to 30 days.
- 20 seconds at 250°C

All ageing started after 1 month of film curing.
The FTIR measurements on paints fragments (from paintings and from mock-ups) have been carried out by sampling the painting layers (at different intervals in the case of aged mock-ups) and using a diamond anvil cell (High Pressure Diamond Optics, Inc.) in transmission modality.
FTIR transmission spectra (64 scans) recorded using a diamond anvil cell were obtained on a Bruker Vertex 70 spectrophotometer coupled with a Bruker Hyperion 3000 IR microscope equipped with an MCT detector (Infrared Associates Inc.), working in the spectral range from 4000 to 600 cm^{-1} with an average spectral resolution of 4 cm^{-1}.
The silicon wafer paints were analysed in the optical bench in transmission modality in the range 4000-400 cm^{-1}.
FT-IR imaging/mapping measurements have recorded on the same instrument equipped, in this setup, with a photovoltaic mercury cadmium telluride (MCT) FPA (Focal Plane Array) detector, Santa Barbara Infrared Inc., working in a spectral range from 4,000 to 900 cm^{-1} (64 scans) with an average resolution of 4 cm^{-1}. The detector consists in a quadratic (128×128) raster of detector elements for an effective operative matrix of 64×64 pixels, and an investigated area of 150 μm

×150 μm operating with a 15x objective. The measurements have been carried out on thin films applied on the silicon wafers.

Results and discussion

This study starts from some evidences observed during conservative interventions on three easel paintings. The first a 201x214 cm oil on canvas from XVII century (Birth of Mary, Antonio Molinari, Church of Ospedaletto, in Venice) exposed to overheating because of a fire. The huge amount of metal soaps found on the blackened surface suggested a possible fast, even if extreme, way to induce the carboxylates formation on mock-ups (see figure 1). The second is a Balla's masterpiece "Grido dimostrazione in piazza del Quirinale" on which the presence of metal soaps and zinc oxalates have been pointed out in presence of natural resins and oleoresinous binder (Rava et al. 2013). The third one is a painting on wood panel from XVI century (Pietà with St. Ambrogio and Girolamo, Giovanni Ambrogio Della Torre, Church of Santa Maria Assunta, Paderno d'Adda, 205x148). In this painting, fluorescence (see figure 2) and FTIR spectra pointed out in particular areas the presence of different signals not referable only to the presence of drying oil and its decay products.

Fig. 1. FT-IR spectra reported show the correspondence between the mock-up of stand oil and lead white heated for 20 seconds at 250°C (red line) with a sample coming from the painting on background exposed to a fire (white line). The yellow spectrum belongs to the mock-up before the heating.

Fig. 2. Detail of a painting on wood panel after the varnish removal (a: visible light; b: UV fluorescence). Violet spectrum is related to the upper part of the glove while the red one to the lower and fluorescent part.

Figure 2 (b) shows a detail of the particular differentiate fluorescence of the glove (the lower part of the glove has a particular orangish fluorescence) still present even after the removal of the varnish. In visible light and under the microscope observation there is no trace of retouching or discontinuity in the red painting layer of the glove presenting the two different fluorescences. Nevertheless, FTIR analyses of two superficial samples coming from the two areas, after the varnish removal, showed two completely different situations. The upper part of the glove (figure 2, violet spectrum) shows the typical spectrum of an aged oil painting: a layer very poor of binder with strong signal coming from the stretching of carbonate of lead white and the band of related carboxylates. The lower part of the glove (figure 2, red spectrum) presents a different superficial composition rich in natural resin (shoulder at 1712 cm^{-1}) and oxalates (sharp band at 1320 cm^{-1}) and

probably resin soaps (broad band at 1540 cm^{-1}). Such in the case of Balla's painting, where only the oil is present (the upper part), no traces of oxalates have been found .

It is very probable that something happened between the original varnish and the substrate only in that area promoting the formation of oxalates and resin soaps since, very unlikely, the author changed the composition of the binder only for the lower part of the gloves Two hypotheses for the differences in surface composition in the glove can be formulated: a resin "glaze", in order to obtain a particular shadows effect is no more detectable since, nowadays, no aesthetical evidences can be clearly pointed out in visible light. A second hypothesis is that a different cleaning "history" interested the glove causing two different conservative situations: an area locally cleaned many times involving the saint face and chest casually including the upper part of the glove, and an uncleaned area in the lower part of the glove, were the resin has been longer in contact with the pigment. This suggests, in both cases, that natural resins are actively involved in the soaps and oxalates formation. So far, this experimentation aimed at demonstrating that terpenic acids coming from the resins can form soaps with cations from pigments in a similar way as fatty acids coming from oil.

Results on aged mock-ups confirmed that natural resins can easily react with some pigment forming metal soaps and, in case of photo-oxidative ageing, oxalates (see figure 3). The specific carbonyl absorption MIR bands of these resin soaps are at very similar wavenumbers of the carboxylates coming from drying oil (1590 cm^{-1} with zinc white, 1568 cm^{-1} with smalt and 1580 cm^{-1} with azurite). In figure 3, spectra of the three considered natural resins mixed with smalt show in all cases the formation of a band (1568 cm^{-1}) referable to the metal soaps formation after 900 hours of simulated solar irradiation. Colophony (red line in figure 3) seems to be the most decayed resin with the almost complete disappearing of methylenic (2920 and 2850 cm^{-1}) and carbonyl (1708 cm^{-1}) bands and the appearing of C-O stretching signal related to the oxalate formation at 1320 cm^{-1}. It has been not possible to identify the nature of oxalates since only the signal at 1320 cm^{-1} was detectable. This behaviour of resins is very similar even in the case of zinc white pigment, another very reactive pigment where the formation of zinc oxalates and zinc resin soaps has been assessed (Poli et al. 2014) such in the case of Balla's painting.

Fig. 3. Spectra of shellac (blue line), dammar (green line) and colophony (red line) mixed with smalt after 900 hours of photo-oxidative ageing.

Interaction of zinc oxide leads to a significant formation of zinc oxalates confirmed by the characteristic carbonyl stretching band at 1363 cm^{-1} together with the C-O stretching band at 1320 cm^{-1} indicating the presence of bridging oxalates, with all four oxygen ions co-ordinated to the metal ions (Gabal et al. 2003). A minimal formation of oxalates has been observed in all the photo-oxidized samples containing resins and some pigments (smalt, zinc white, lead white and azurite) but never in

the case of stand oil samples. This is particularly evident in the samples containing colophony and shellac.
It is important to point out that in presence of smalt and zinc oxide the formation of metal soaps is unmistakable within all the resins few day after the film casting even without any accelerated ageing. The fast kinetic of smalt with natural resins means that potassium ions become rapidly available in sufficient amount. Moreover, this means that terpenic acids, seizing cations from pigment grains to form metal soap, can work together with fatty acids from oil favouring the discolouration of smalt in the cases of varnished paintings. Probably resins are more reactive than oil because most of terpenic acids are immediately available while in the case of oil most of the fatty acids became available after the hydrolysis of the triglycerides.
Red earth and umber earth show a minimal amount of soap formation (1548 cm^{-1}). Differences between the two iron based pigments, a higher reactivity of umber earth, are probably related to the content of the manganese since pure iron oxides (used as reference) did not showed any metal carboxylate formation in the considered ageing conditions; on the contrary these earth pigments looking at infrared spectra, seem to show a slightly protective effect from photo-oxidation of the terpenic structures. Titanium white, as predictable, is pretty stable and do not induce the formation of any soap but seems to favour the oxidative processes.
The behaviour of lead white, one of the most reactive pigments with drying oil, resulted particularly interesting showing a minimal interaction with the resins. Only after the thermo-oxidative ageing (20 seconds at 250 C°) a reactivity similar to the drying oil has been showed, i.e. the almost complete transformation of the organic binder in metal soaps (see figure 1) with the appearing of the carboxylates band at 1528 cm^{-1}.
Azurite proved to be stable even if, in few samples, grain of discoloured pigment and rich in resin soaps have been found (see figure 4) by means of micro FT-IR localized measurements. Only on the green grain, a well-defined band of carboxylates (at 1594 cm^{-1}) is clearly detectable (fig. 4, green spectrum). In all the other areas of the chemical image and in the diamond anvil cell measurements, the obtained spectra do not show a detectable carboxylates band (fig. 4, blue spectrum) or present only a shoulder probably referable to soaps (fig. 4, red spectrum).

Fig. 4. Chemical image of azurite grains in colophony medium integrated in the spectral range from 1550 to 1600 cm^{-1}. Only the green grain appears surrounded by metal soaps in the chemical image.

Considering the low average reactivity showed by azurite with resins in the mock-ups, it is not clear if the observed colour loss (the green grain in figure 4) is a consequence of the saponification process or if the soap formation occurred on a previously decayed and more reactive grain contained in the azure pigment powder. It

is important to point out that the complex carbonate bands of azurite can disguise the eventual carboxylate signals if weak for the low concentration.
All the considered ageing conditions induced similar effects but the thermo-oxidative one (25 seconds at 250 C°) that forced, as predictable, an extended decay of the organic component and a huge formation of metal soaps. In figure 1 you can see that spectrum coming from a sampling on the blackened surface is really comparable to the one obtained with a mock-up heated at 250 C° for 25 seconds. This extreme accelerated ageing has been included to confirm that overheating can be a significant cause of metal soaps formation. No oxalate formation has been observed. The lowest effective ageing has been the thermal one (50°C, 1100 h) that induced less soaps formation than the room conditions. This is probably related to the very low humidity content in the fan-assisted oven and to a faster drying with the consequent reduction of mobility of the system.

Conclusions

In this contribute, the possibility of metal soaps formation in presence natural resin and pigments has been assessed. Terpenic acids quickly react with cations coming from some pigments in order to form carboxylic salts as resin soaps. Smalt and zinc white were the most reactive pigments immediately forming metal carboxylates, even without any ageing; also azurite and natural earths proved to be slightly reactive. The rapid soap formation of resins in presence of smalt point out as terpenic acids can favour the leeching of potassium ions contributing, together with fatty acid from drying oil to the discolouration in varnished easel paintings. Lead white showed a lower affinity to the natural resins than to stand oil. This will be confirmed testing lead white with different content of cerussite and hydrocerussite and other lead pigments such as lead oxides (minium).
The ability of natural resins in metal soaps forming means that, at least at the interface could also occur unpredicted competitive reactions among fatty acids coming from the oil painting layer and terpenic acids coming from the varnish. Oil metal soaps coming from the painted layer could, for example, exchange of cations with terpenic acids when they reach the varnish playing a role in the superficial crusts formation. Generally, they could affect aggregation and the ionomeric structure.
Particularly interesting is the oxalate formation observed in the most of samples containing metal soaps active pigments and natural resins aged in photo-oxidative conditions. It has been possible to define the oxalate cation only in the case of samples containing zinc white. The oxalate formation during the resins ageing in presence of reactive pigment could be an explanation of the strange superficial behaviour reported in the example in figure 2 where the oxalate formation has been observed only in the area where natural resin is still present. Results allow to hypothesize that the hard to clean thin oxalate patinas frequently found under varnishes in easel paintings can be related to resin degradation more than to drying oil

A new experimentation is going on in order to include new pigments and natural resins but also to confirm the obtained results, in particular the ones related to the oxalate formation. This is very important since the presence of oxalates deeply affects the cleaning processes. The new ongoing experimentation is focused on:

- Understand why natural resins have different behaviours (acidity, free acid amounts and mobility);
- Test oleoresinous binders and possibly study the results of competition between fatty and terpenic acids;
- Understand if the different reactivities are related to a particular affinity of specific terpenic acids with cations, or to the ability of one of the resin components to modify a pigment's chemistry increasing the cation availability.

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